

Enantiomeric amplification of amino acids: part 11 –spontaneous resolution in a porous environment

Royal Truman, Chris Basel, and Stephen Grocott

Spatial separation of D- and L-amino acid (AA) enantiomers would be easier if homochiral crystals formed than when in solution. Experiments using capillary motion of aspartic acid (Asp) and glutamic acid (Glu) solutions through porous brick produced a mixture of D and L crystals. These were intimately mixed and thus could not explain how only L-AAs would have been used to form proteins prebiotically. Furthermore, the experiments used: 1) pure water instead of a saline solvent; 2) AA concentrations many orders of magnitude higher than realistic; 3) excluded contaminants; and used 4) a clean brick having suitable cavity sizes. A natural brine environment would have had none of these characteristics. Trapped in solid form, Asp and Glu could not have formed peptides, but redissolution would have regenerated the racemic solution.

We continue here with part 11 of a series of papers that critique proposed natural explanations for the abiogenetic origin of pure L-amino acids (AAs). Bonner championed the theory that spontaneous resolution of D and L crystals would offer the best natural terrestrial mechanism for separating D- and L-AAs.¹ Only L-AA enantiomers must be used to form biological proteins. However, about 90% of AAs form racemic crystals at moderate temperatures, which therefore never spontaneously resolve.²⁻⁶

In several experiments discussed below, origin of life (OoL) researcher Viedma examined solutions of aspartic acid and glutamic acid, arguing that these AAs have been identified in samples from the Murchison meteorite. These two AAs were each found at concentrations of only ~1 ppm, though, of which the amount of terrestrial contribution was unknown.⁷ Furthermore, AAs found on some meteorites are usually bound within larger complex molecules which must be extracted through vigorous acid hydrolysis.⁸

Viedma also mentioned that these two AAs are among the most abundant formed in experiments simulating the primitive earth.³ However, he overlooked that, in the paper he referenced, Sidney Fox correctly disparaged the notion of lightning acting in the atmosphere under necessarily but geologically implausible hydrogen-rich conditions and the experimental use of electric discharges in closed containers.⁹

Enantiomer enrichment in porous solid environments

Viedma reported, in 2001, that racemic mixtures of aspartic acid and of glutamic acid can be caused to form homochiral crystals mixed in equal proportions (i.e., *conglomerates*) at ambient temperature.³ However, their usual behaviour is to form *racemic compounds* (which consist of D and L enantiomers intimately combined within each crystal) to first crystallize from solution.

Forming the homogenous crystals was not easy. In the first series of experiments, 10 g of either racemic aspartic acid or glutamic acid was dissolved in 1 litre of water, constantly stirred, and heated to 80°C for 30 min to ensure complete dissolution. 50 mL samples were extracted and allowed to cool to permit crystals to grow. The initial concentration was too low, and crystals were not produced. Therefore, the solution was concentrated by evaporation.³ When aspartic and glutamic AAs were crystallized from free aqueous solutions, however, only racemic DL-aspartic and DL-glutamic AA crystals were produced.

Remarkable crystallization processes were known to occur in porous media.¹⁰ Therefore, Viedma carried out another set of experiments using a porous insulating fire brick, partially immersed in the 10 g / L of each AA to cause capillary rise, as illustrated in figure 1.

Water was evaporated and aspartic or glutamic acid crystals were found in a narrow upper zone inside the porous brick. *Contra* the results from simply evaporating solutions, these crystals formed conglomerates; i.e.,

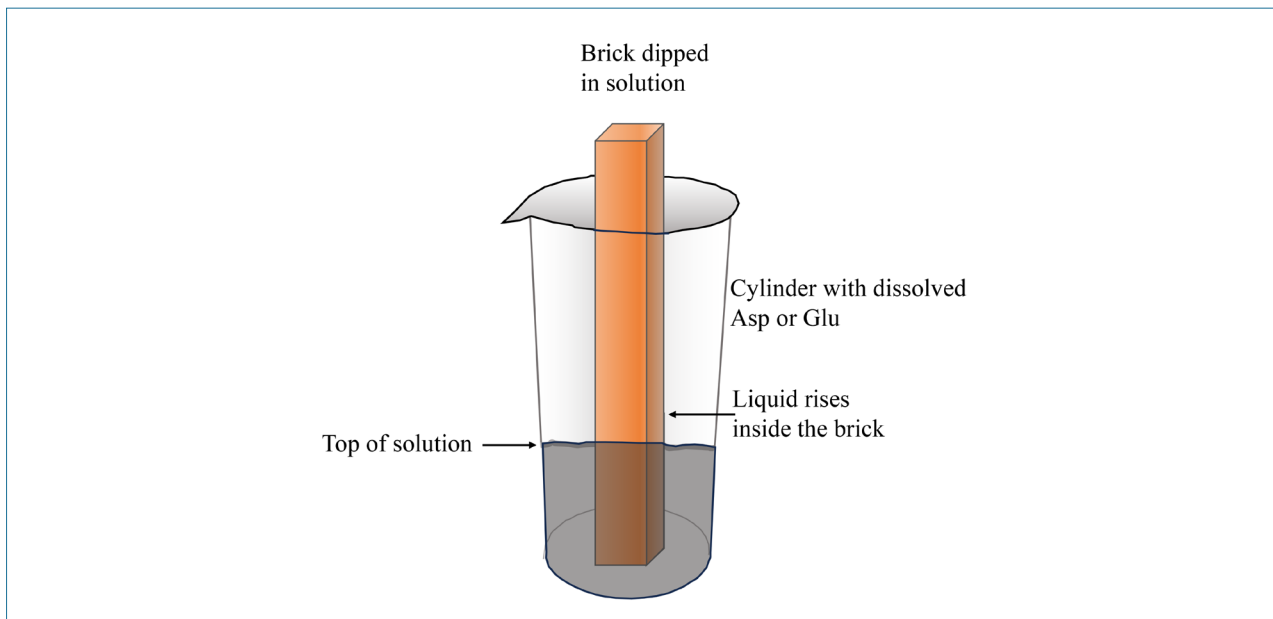


Figure 1. A fire brick was dipped into aqueous solutions of aspartic acid or glutamic acid. Homochiral crystals were formed after capillary rise inside the brick.³ Original figure created by Royal Truman.

the individual crystals consisted of only D or only L enantiomers, mixed in identical amounts.³

This is a case of polymorphism, involving two phases ($D_{crystal} + L_{crystal}$) and $DL_{crystal}$. Because the racemic crystals were more stable than enantiomeric conglomerates, the free energy change for the transformation:



is negative. Therefore, the D-only and L-only crystals obtained were metastable with respect to racemic DL crystals.³

Why did separate D and L crystals form in porous media, resulting in a far-from-equilibrium outcome? It is well known that crystals resulting from high supersaturation can behave abnormally, giving rise to metastable (i.e., kinetically stable) phases, for several possible reasons.^{3,11,12} This seems to be an example of Ostwald’s Rule, which expresses that often the first solid formed upon crystallization of a solution or a melt is the least stable polymorph, which is kinetically favoured, rather than the thermodynamically favoured form(s) that are created later.^{13–15} Maximum supersaturation depends on factors such as temperature, stirring and mechanical shock, thermal history, and total mass of solution. The limited particle mobility in a porous media provided a range of high supersaturation levels, as compared to the crystallization in free solutions.³

Since, in the most probable natural environments, evaporation of water containing an AA did not yield the

results wished for, a new naturalist narrative had to be invented. The conditions of the latter experiments were claimed to mimic a sedimentary environment such as a dry lakebed where capillary rise of saline ground water might occur.

Viedma does admit the obvious, that this spontaneous resolution mechanism over time will produce an equal number of opposing AA resolutions. Therefore, no net increase in enantiomeric excess could have occurred.

Critique of these studies

- The evaporation experiments allegedly “mimic a sedimentary environment such as a playa where one may expect capillary rise of saline ground water”. However, in contrast to this, pure Asp or Glu was dissolved in doubly *distilled water* instead of a saline solution.
- Proteins require many additional kinds of L-AAs whose enantiomers didn’t resolve under these conditions.
- 10 g / L solutions of Asp and Glu are many orders of magnitude more concentrated than putative prebiotic conditions would have been. Leading OoL researcher Professor Bada estimated that the maximum concentration of AAs in ancient oceans would have been only $\sim 10^{-8}$ g / L water.¹⁶ Viedma’s solutions were a billion times more concentrated than this. Asp and Glu crystals could not have formed from concentrations many orders of magnitude lower. Evaporation of extremely dilute solutions would have distributed any

Asp or Glu contained over vast distances, so redissolving them would have produced very dilute solutions of Asp and Glu.¹⁷

- Ocean water currently contains, on average, about 35 g of salts / L.¹⁸ Asp and Glu produced today or on a primordial earth through natural chemical processes could only represent an insignificant proportion of the highly contaminated saline ground water. Pristine bricks having suitable cavities for crystallization to occur were placed into solutions of an AA. A continuous flow due to capillary action and a source of extremely concentrated Asp or Glu was ensured. The clean laboratory glass vessel prevented dilution and contamination. These factors cannot be compared to a primordial slurry of innumerable substances.
- Furthermore, even if Asp and Glu crystals had formed, they would have been encased in a solid cement-like environment. They could not have formed peptides unless the crystals redissolved in water, where they would have regenerated a racemic solution. Any temporary periods of warming, due to volcanic action, meteorite impacts, etc. would have facilitated extraction and dissolution of the crystals.
- Any L and D crystals formed would be in identical proportion and intimately mixed spatially. This would not have led to peptides of only L enantiomers.

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17. Bada's estimate of $<10^{-8}$ g/l AA in water is equivalent to 1 g in a water volume $1 \text{ km} \times 100 \text{ m} \times 1 \text{ m}$. Therefore, any dissolved Asp or Glu would have been widely distributed upon evaporation of the water.
18. According to Wikipedia and the United States Geological Survey, one litre of ocean water contains, on average, about 35 g of salts. [Why is the ocean salty?](#) usgs.gov, accessed 14 Nov 2022.

Royal Truman has bachelor's degrees in chemistry and in computer science from State University of New York; an M.B.A. from the University of Michigan (Ann Arbor); a Ph.D. in organic chemistry from Michigan State University; and a two-year post-graduate 'Fortbildung' in bioinformatics from the Universities of Mannheim and Heidelberg. He works in Germany for a European-based multinational.

Chris Basel has a bachelor's degree in chemistry from William Jewell College, a master's degree in analytical chemistry from the University of Kansas, and a certificate in ADMET Process (pharmacology) from the University of California-San Diego. He worked as a research manager in the pharmaceutical industry for 30 years and now serves as an associate professor of chemistry and department chair at a Christian university in Missouri.

Stephen Grocott has 1st Class Honours and Ph.D. degrees in organometallic chemistry (chiral metal complexes). Currently, he is managing director with an advanced chemicals manufacturing business. Before that, he was the lead processing technology expert for some of the world's largest resource companies. He is an adjunct professor with a large Australian university and was the chair of the board of the world's largest non-profit minerals R&D organisation. He has also served on the board of Youth for Christ Australia.